

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Application of

Applicant(s) : A. Faur-Ghenciu
Serial No. : 10/803,799
Filed : March 18, 2004
Title : HIGH ACTIVITY WATER GAS SHIFT CATALYSTS WITH
NO METHANE FORMATION
Docket No. : GMC 0026 PA/42320.30/GP-302810
Examiner : W. Langel
Art Unit : 1754

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JAN 30 2006

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

DECLARATION OF ANCA FAUR-GHENCIU, SAILESH MULLAPUDI,
MARK R. FEAVIOUR, NATHAN E. TRUSTY, AND JESSICA G. REINKINGH
UNDER 37 C.F.R. 1.131

Anca Faur-Ghenciu, Sailesh Mullapudi, Mark R. Feaviour, Nathan E. Trusty, And Jessica G. Reinkingh, the applicants in the above-identified patent application, declare as follows:

1. We are the inventors of claims 1-44 of the above-identified patent application and inventors of the subject matter described and claimed therein.
2. Prior to December 20, 2002, we reduced the claimed invention to practice as evidenced by Exhibits A-D attached hereto.
3. Exhibit A is a copy of an email from inventor Anca Ghenciu to Maeve Carney, Peter Fray, and Ian Wishart of Johnson Matthey PLC with an attachment showing a three page draft of the Record of Invention for the present invention. The draft Record of Invention shows a brief description of the invention, testing conditions, various formulations, results and

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Serial No. 10/803,799
Docket No. GMC 0026 PA / 42320.30/GP-302810

conclusions, and supporting data.

4. Exhibit B is a copy of another email from inventor Anca Ghenciu to Maeve Carney, Peter Fray, and Ian Wishart of Johnson Matthey PLC with an attachment showing a three page corrected draft of the Record of Invention for the present invention. The corrected draft Record of Invention shows a brief description of the invention, testing conditions, various formulations, results and conclusions, and supporting data.

5. Exhibit C is an email from inventor Anca Ghenciu to Maeve Carney, and Peter Gray of Johnson Matthey PLC with an attachment showing an updated four page Record of Invention. The updated draft Record of Invention shows a brief description of the invention, testing conditions, various formulations, results and conclusions, and supporting data.

6. Exhibit D is an email from Peter Gray of Johnson Matthey PLC to James Saller of General Motors Corporation, the assignee of the present invention, with an attachment forwarding the Record of Invention for the present invention. The Record of Invention shows a brief description of the invention, testing conditions, various formulations, results and conclusions, and supporting data.

7. Each of the dates deleted from Exhibits A-D is prior to December 20, 2002. All work relating to the conception and reduction to practice of this invention was carried out in the United States and the United Kingdom, a WTO member country.

The declarants further state that the above statements were made with the knowledge that willful false statements and the like are punishable by fine and/or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of this application or any patent resulting therefrom.

Serial No. 10/20/799

Docket No. 0316.0036 PA / 42320.30/GP-302810

Date: _____

Anca Faur-Obenhu

Date: _____

Sailash Mulpudi

Date: _____

Mark R. Fenwick

Date: 1/27/06

Nathan R. Trusty

Date: _____

Jessica G. Reinkingh

Prior, Patricia

From: Anca Ghenciu [ghencia.EP.DEVON@matthey.com]
Sent:
To: Maeve Carney; Peter Gray; Ian Wishart
Cc: Mike Petch
Subject: Re: INT: Preparation of RoI's for GM

Attachments: Ptgroup-CeZrLa.doc

RoI_Cu-Mn-Co-promoted-



RoI_Cu-Mn-Co-promoted-Ptgroup-...

Dear all,

Attached are the WGS RoI's based on the list of concepts (GM RoI request, attached). Following the suggested pattern, I have generated the two RoI's attached, with the observation: position #10 in the RoI request includes two large concepts: promoters and Ce:Zr ratios, each of them could be a stand alone RoI. It may be a good idea to split this in two, per concept, as it was first originated.

Best wishes,

Anca

>>> Peter Gray >>>
Program: GM fuel processing sub program
Topic: Preparation of RoI's for GM

Dear All,

GM have selected a list of concepts from the list of intellectual properties presented during the meeting. Would you arrange preparation of Records of Invention (ROIs) for your relevant areas. I have attached a document outlining the concepts GM are interested in, for patents and for publications.

Jim Saller has requested that related concepts should be combined into one ROI, as appropriate.

Jim has also said that the internal Record of Invention form used by JM (attached) would be suitable for recording the above listed inventive concepts. The inventive concept should be adequately described and additional supporting documentation should be included with the record of invention. Feel free to make the RoI as long as necessary (GM are expecting more than a single page RoI).

Jim would like to have the status of these proposed Records of Invention reviewed during up-coming meetings, so it would be good if we could have a first draft of these RoI's by the next GM meeting ().

Please discuss with Ian/Maeve when preparing the RoIs. Thanks.

Peter



**Johnson Matthey Fuel Cells***the power within***RECORD OF INVENTION****Title of Invention: High Activity Water Gas Shift Catalysts with No Methanation Activity.****Record Written by: Anca Ghenciu****Date Record Written:**

Brief Description of Invention: In the catalyzed water gas shift (WGS) reaction, WGS catalyst systems with high WGS activity and no methanation activity, consisting of 1-4% platinum and ceria or ceria-zirconia mixed oxides, said catalysts including promoters or dopants incorporated on/in the oxide lattice and comprising of 0.1%-10% copper, or 0.1%-10% manganese, or 0.2-20% lanthanum, said catalysts tested in the presence of carbon monoxide, water, carbon dioxide and hydrogen, at 200°-475°C, preferably 275°-425°C. The invention also relates to the use of said catalysts as coated on monolithic supports for the WGS reaction.

Catalyst testing: fixed bed reactor, 1 g catalyst and 1 g cordierite 45-60 mesh, under the following reaction conditions: 8%CO, 30%H₂O, 10%CO₂, 32.5%H₂, 1%CH₄, balance N₂, in a fixed bed reaction system, at 67,500 cc/g cat /hr weight hourly space velocity, between ~150 and ~600°C. Test results in each case (Examples) to be written.

Formulations:

- Cu- or Mn- or Co-promoted Pt/CeO₂;
- Cu- or Mn- or Co-promoted Pt/LaOx-CeO_y (several ratios lanthana:ceria)
- Cu- or Mn- or Co-promoted Pt/CeO₂-ZrO₂ (several ratios ceria:zirconia) (Mn either as added promoter or as part of the ceria-zirconia oxide lattice)
- CuOx-CeOx (Cu:Ce 20:80)
- Pt/LaOx-CeOx where La is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.
- To add Fe to the above (if results confirm)

All the above formulations are highly active catalysts for the WGS reaction with no methane formation over a large temperature range (200-600°C).

Results and conclusions:

1. The "anti-methanation" element(s) can be added as surface promoters or as dopants, i.e., incorporated in the oxide lattice upon preparation of the oxide.
2. In the case of Mn (and possibly Fe) promoted formulations, the catalysts are also expected to be more durable against irreversible reduction based on the re-oxidizing ability conferred by the redox elements in the presence of water.
3. The platinum - ceria-zirconia mixed oxides show improved catalytic performance over ceria-lanthana, also over ceria- or zirconia-only. (here refer to previous WGS Rol)

4. For the Pt/LaOx-CeOx, lanthanum is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.

Novelty of the Invention: Under the reaction conditions chosen for testing: 1. High activity catalysts for medium temperature range WGS reaction, at 200°-475°C with no methanation activity even at temperatures higher than 475°C. 2. Cu-, or Mn-, or Co-promoted (or combinations thereof) Pt - ceria-zirconia, Pt-ceria-lanthana, or Pt-ceria catalysts with high WGS activity and no methane formation over a large temperature range (200-600°C). 3. Impact of the preparation method of La-doped ceria for suppression of methanation reaction (possibly the impact of lanthanum carbonate on the suppression of methane formation under WGS reaction conditions). 4. Possibly add the effect of Fe and/or promotion with both alkali metals (see previous Rol) and redox elements for methanation suppression and

Benefit of Invention: 1. Catalyst formulations with high WGS catalytic activity and with no methanation activity. 2. Suppression of methane formation on platinum-ceria-zirconia, or platinum-ceria-lanthana, or platinum-ceria, under WGS reaction conditions, by promotion with Cu, Mn, Co, or combinations thereof. Use of CuOx-CeOx oxides for WGS.

References to Supporting Work (e.g. Lab Notebook Number): most significant data is listed

1757-132-3	(1%Pt-0.5%Cu)/75%La2O3-25%CeO2
1757-138-3	(1%Pt-0.5%Cu)/ 25%La2O3-75%CeO2
1757-145-13	(1%Pt-0.5%Cu)/CeO2
1757-144-15	(1%Pt-0.5%Cs-0.5%Cu)/CeO2 (also refer to previous WGS Rol – here combined effect Cs-Cu)
C480-96A	1%Pt/LaOx-CeOx
1757-4-149-1A	1%Cu/2.5%Pt/CeO2 –
1757-4-149-2A	0.5%Cu/2.5%Pt/CeO2 –
1757-4-149-3A	2.5%Cu/2.5%Pt/CeO2 –
1875-001	(1%Pt-5%Cu)/CeO2 –
1875-002	(1%Pt-10%Cu)/CeO2 –
1875-003	10%Cu/CeO2 –
1875-007	CuOx-CeOx (Cu:Ce ~20:80 wt) –
1875-011	CuOx-CeOx (Cu:Ce ~50:50 wt) –

other records are to be listed

1944-001 2%Pt/0.2%Cu/CeO₂-ZrO₂ (19.6 : 80.4 wt) –

1944-017 2%Pt/0.2%Cu/CeO₂-ZrO₂ (58 : 424 wt) –

1944-019 0.2%Cu/2%Pt/CeO₂-ZrO₂ (58 : 424 wt) –

1944-011 10%Cu/ CeO₂-ZrO₂ (58 : 42 wt) –

1944-003 2%Pt/0.6%Mn/CeO₂-ZrO₂ (19.6 : 80.4 wt) –

1944-057 2%Pt/1%Co/CeO₂-ZrO₂ (58 : 42 wt) –

Also to be added: series of samples promoted with Mn (several Mn %) –
Fe-promoted and doped CeZr records – to be added.

Contributors to the Invention: A. Ghenciu, M. Feaviour, N. Trusty, J Reinkingh

If Invention has been discussed with or disclosed to external third parties, give details:

Witness Statement:

"On the date beside my signature, I read and understood the above invention"

Name:

Signature:

Date:

Prior, Patricia

From: Anca Ghenciu [ghencia.EP.DEVON@matthey.com]
Sent:
To: Maave Carney; Peter Gray; Ian Wishart
Cc: Mike Petch
Subject: Re: INT: Preparation of Rol's for GM
Attachments: Rol_Cu-Mn-Co-promoted-Ptgroup-CeZrLa.doc; I



Rol_Cu-Mn-Co-pr
moted-Ptgroup-...

I am resending the WGS Rol's with a few corrections (highlighted in blue). Please

disregard the previous files.

Thank you,
Anca



**Johnson Matthey Fuel Cells***the power within***RECORD OF INVENTION**

Title of Invention: High Activity Water Gas Shift Catalysts with No Methanation Activity.

Record Written by: Anca Ghenciu

Date Record Written:

Brief Description of Invention: In the catalyzed water gas shift (WGS) reaction, WGS catalyst systems with high WGS activity and no methanation activity, consisting of 1-4% platinum and ceria or ceria-zirconia mixed oxides, said catalysts including promoters or dopants incorporated on or in the oxide lattice and comprising of 0.1%-10% copper, or 0.1%-10% manganese, or 0.5%-5% Co, or 0.2-15% lanthanum oxide, said catalysts tested in the presence of carbon monoxide, water, carbon dioxide and hydrogen, with maximum activity at 200°-475°C, preferably 275°-425°C. The invention also relates to the use of said catalysts as coated on monolithic supports for the WGS reaction.

Catalyst testing: fixed bed reactor, 1 g catalyst and 1 g cordierite 45-60 mesh, under the following reaction conditions: 8%CO, 30%H₂O, 10%CO₂, 32.5%H₂, 1%CH₄, balance N₂, in a fixed bed reaction system, at 67,500 cc/g cat /hr weight hourly space velocity, between ~150 and ~600°C. Test results in each case (Examples) to be written.

Formulations:

- Cu- or Mn- or Co-promoted Pt/CeO₂;
- Cu- or Mn- or Co-promoted Pt/LaOx-CeO_y (several ratios lanthana:ceria)
- Cu- or Mn- or Co-promoted Pt/CeO₂-ZrO₂ (several ratios ceria:zirconia) (Mn either as added promoter or as part of the ceria-zirconia oxide lattice)
- CuOx-CeOx (Cu:Ce 20:80)
- Pt/LaOx-CeOx where La is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.
- To add Fe to the above (if results confirm suppression of methanation with Fe)

All the above formulations are highly active catalysts for the WGS reaction with no methane formation over a large temperature range (200-600°C).

Results and conclusions:

1. The "anti-methanation" element(s) can be added as surface promoters or as dopants, i.e., incorporated in the oxide lattice upon preparation of the oxide.
2. In the case of Mn (and possibly Fe) promoted formulations, the catalysts are also expected to be more durable against irreversible reduction based on the re-oxidizing ability conferred by the redox elements in the presence of water.
3. The platinum - ceria-zirconia mixed oxides show improved catalytic performance over ceria-

lanthana, also over ceria- or zirconia-only. (here refer to previous WGS Rol)

4. For the Pt/LaOx-CeOx, lanthanum is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.

Novelty of the Invention: Under the reaction conditions chosen for testing: 1. High activity catalysts for medium temperature range WGS reaction, at 200°-475°C with no methanation activity even at temperatures higher than 475°C. 2. Cu-, or Mn-, or Co-promoted (or combinations thereof) Pt - ceria-zirconia, Pt-ceria-lanthana, or Pt-ceria catalysts with high WGS activity and no methane formation over a large temperature range (200-600°C). 3. Impact of the preparation method of La-doped ceria for suppression of methanation reaction (estimated to be due to a lanthanum carbonate/hydroxy-carbonate phase). 4. Use of CuOx-CeOx oxides for WGS.

Benefit of Invention: 1. Catalyst formulations with high WGS catalytic activity and with no methanation activity over a large temperature range. 2. Suppression of methane formation on platinum-ceria-zirconia, or platinum-ceria-lanthana, or platinum-ceria, under WGS reaction conditions, by promotion with Cu, Mn, Co, or combinations thereof.

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1757-4-149-3A	2.5%Cu/2.5%Pt/CeO2 –
1875-001	(1%Pt-5%Cu)/CeO2 –
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1875-003	10%Cu/CeO2 –
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other records are to be listed

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Also to be added: series of samples promoted with Mn (several Mn %) –
Fe-promoted and doped CeZr records – to be added.

Contributors to the Invention: A. Ghenciu, M. Feaviour, N. Trusty, J Reinkingh

If Invention has been discussed with or disclosed to external third parties, give details:

Witness Statement:

"On the date beside my signature, I read and understood the above invention"

Name:

Signature:

Date:

Prior, Patricia

From: Anca Ghenciu [ghencia.EP.DEVON@matthey.com]
Sent:
To: Maeve Carney; Peter Gray
Subject: updated RoIs

Importance: High

Attachments: . RoI_Cu-Mn-Co-promoted-Ptgroup-CeZrLa.doc



RoI_Cu-Mn-Co-pro
moted-Ptgroup-... ** High Priority **

Peter, Maeve,

Updated RoI's as of - attached. There are more materials, but the most important records (with dates) are included. The reaction tests will be included in the patent version in due course, in examples. I have created a database with all catalyst records in the program, so it should be easy to follow from now on.

Anca



**Johnson Matthey Fuel Cells***the power within***RECORD OF INVENTION****Title of Invention:** High Activity Water Gas Shift Catalysts with No Methanation Activity.**Record Written by:** Anca Ghenciu**Date Record Written:**

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- CuOx-CeOx (Cu:Ce 20:80 – 50:50)
- Pt/LaOx-CeOx where La is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.

All the above formulations are highly active catalysts for the WGS reaction with no methane formation over a large temperature range (200-600°C).

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3. The platinum - ceria-zirconia mixed oxides show improved catalytic performance over ceria-lanthana, also over ceria- or zirconia-only. (here refer to previous WGS Rol)

4. For the Pt/LaOx-CeOx, lanthanum is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.

Novelty of the Invention: Under the reaction conditions chosen for testing: 1. High activity catalysts for medium temperature range WGS reaction, at 200°-475°C with no methanation activity even at temperatures higher than 475°C. 2. Cu-, or Mn-, Co-, or Fe-promoted (or combinations thereof) Pt - ceria-zirconia, Pt-ceria-lanthana, or Pt-ceria catalysts with high WGS activity and no methane formation over a large temperature range (200-600°C). 3. Impact of the preparation method of La-doped ceria for suppression of methanation reaction (estimated to be due to a lanthanum carbonate/hydroxy-carbonate phase). 4. Use of CuOx-CeOx oxides for WGS.

Benefit of Invention: 1. Catalyst formulations with high WGS catalytic activity and with no methanation activity over a large temperature range. 2. Suppression of methane formation on platinum-ceria-zirconia, or platinum-ceria-lanthana, or platinum-ceria, under WGS reaction conditions, by promotion with Cu, Mn, Co, Fe or combinations thereof.

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1757-4-149-2A	0.5%Cu/2.5%Pt/CeO2 -
1757-4-149-3A	2.5%Cu/2.5%Pt/CeO2 -
1875-001	(1%Pt-5%Cu)/CeO2 -
1875-002	(1%Pt-10%Cu)/CeO2 -
1875-003	10%Cu/CeO2 -
1875-007	CuOx-CeOx (Cu:Ce ~20:80 wt) -
1875-011	CuOx-CeOx (Cu:Ce ~50:50 wt) -
1757-188A	2%Pt/Fe-CeO2 -

1944-001	2%Pt/0.2%Cu/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-017	2%Pt/0.2%Cu/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-019	0.2%Cu/2%Pt/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-011	10%Cu/ CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-003	2%Pt/0.6%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-057	2%Pt/1%Co/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-021	2%Pt/0.2%Cu/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-023	0.2%Cu/2%Pt/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-029	10%Cu/ CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1875-031	2%Pt/(ZrO _x -CeO _x -MnO _x)
1944-025	2%Pt/0.5%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-033	2%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-035	2%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-037	3%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-039	3%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-041	2%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-043	3%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-045	3%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-047	2%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) -
1944-079	2%Pt/2%Co/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-081	2%Pt/1%Fe/CeO ₂ -ZrO ₂ (58 : 42 wt) -
1944-083	2%Pt/(0.5%Fe-0.25%Mn)/CeO ₂ -ZrO ₂ (58 : 42 wt) -

Contributors to the Invention: A. Ghenciu, N. Trusty, M. Feaviour, S. Mullanpudi, J Reinkingh

If Invention has been discussed with or disclosed to external third parties, give details:

Witness Statement:

"On the date beside my signature, I read and understood the above invention"

Name:

Signature:

Date:

Prior, Patricia

From: Peter Gray [grayp.FCHQ.READING@matthey.com]
Sent:
To: saller@gm.com
Cc: oconnell@gm.com; piedmont@gm.com; robb@gm.com; stottler@gm.com;
Wagner@gm.com; Mike Atkinson; Maeve Carney; Sue Ellis; Julia Evans; Jack Frost; Anca
Ghenciu; Graham Hards; Mike Petch; Lu Potter; Jessica Reinkingh; Ros Stayne; Ian Wishart
Subject: EXT: Records of Invention
Attachments: Rol.zip



Rol.zip (1 MB)

Program: GM fuel processing sub program
Topic: Records of Invention

Dear Jim,

Please find attached 19 RoIs for the items listed in your email of . I have listed the concepts from
your email in a summary document (RoI Status.doc), also attached.

Some concepts (7 and 14) have been covered as two RoIs, as they could possibly be regarded as two inventions.

Any concepts you have listed as "possible publication" I have also included as RoIs, just as a convenient way of documenting the ideas.

Would you address specific technical questions on any RoI to the appropriate author. Thanks. For any information on background IP, would you please contact Maeve. As per the MEA program, Maeve is putting together a package of previous JM patents which may be relevant background. She will send this to you next week.

We will be having our next monthly meeting in Honeoye Falls on . I'm planning to schedule
some time in the agenda to allow for further discussion of these RoIs. Do you have a preference for the

Best regards

Peter

IMPORTANT NOTICE

CONFIDENTIAL INFORMATION



This email, including attached documents, contains confidential and proprietary legal, technical or business information relating to the Fuel Cell Research Agreement having the effective date of . This communication is intended only for the use of the person or entity to whom it is addressed. If you are not the addressee, or the person responsible for delivering communications to the addressee, do not read, copy or otherwise distribute the information, but call us on +44 (0)118 9242156 and ask for Ros Stayne, who will advise you how to return this communication or alternatively email frostjc@matthey.com

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**Johnson Matthey Fuel Cells***the power within***RECORD OF INVENTION**

Title of Invention: High Activity Water Gas Shift Catalysts with No Methanation Activity.

Record Written by: Anca Ghenciu

Date Record Written:

Brief Description of Invention:

In the catalyzed water gas shift (WGS) reaction, WGS catalyst systems with high WGS activity and no methanation activity, consisting of 1-4% platinum and ceria or ceria-zirconia mixed oxides, said catalysts including promoters or dopants incorporated on or in the oxide lattice and comprising of 0.1%-10% copper, or 0.1%-10% manganese, or 0.1%-10% Fe, or 0.5%-5% Co, or 0.2-15% lanthanum oxide, said catalysts tested in the presence of carbon monoxide, water, carbon dioxide and hydrogen, with maximum activity at 200°-475°C, preferably 275°-425°C. The invention also relates to the use of said catalysts as coated on monolithic supports for the WGS reaction.

Catalyst testing: fixed bed reactor, 1 g catalyst and 1 g cordierite 45-60 mesh, under the following reaction conditions: 8%CO, 30%H₂O, 10%CO₂, 32.5%H₂, 1%CH₄, balance N₂, in a fixed bed reaction system, at 67,500 cc/g cat /hr weight hourly space velocity, between ~150 and ~600°C. Test results in each case (Examples) to be written.

Formulations:

- Cu- or Mn- or Co- or Fe- promoted Pt/CeO₂;
- Cu- or Mn- or Co- or Fe-promoted Pt/LaOx-CeOy (several ratios lanthana:ceria)
- Cu- or Mn- or Co- or Fe-promoted Pt/CeO₂-ZrO₂ (several ratios ceria:zirconia) (said elements either as added promoters or as part of the ceria-zirconia oxide lattice)
- CuOx-CeOx (Cu:Ce 20:80 - 50:50)
- Pt/LaOx-CeOx where La is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.

All the above formulations are highly active catalysts for the WGS reaction with no methane formation over a large temperature range (200-600°C).

Results and conclusions:

1. The "anti-methanation" element(s) can be added as surface promoters or as dopants, i.e., incorporated in the oxide lattice upon preparation of the oxide.
2. In the case of Mn, Co, and Fe promoted formulations, the catalysts are also expected to be more durable against irreversible reduction based on the re-oxidizing ability conferred by the redox elements in the presence of water.
3. The platinum - ceria-zirconia mixed oxides show improved catalytic performance over ceria-lanthana, also over ceria- or zirconia-only. (here refer to previous WGS Rol)
4. For the Pt/LaOx-CeOx, lanthanum is incorporated in the lattice as an amorphous phase, possibly as "non-stoichiometric" oxycarbonate or hydroxycarbonate.

Novelty of the Invention:

Under the reaction conditions chosen for testing: 1. High activity catalysts for medium temperature range WGS reaction, at 200°-475°C with no methanation activity even at temperatures higher than 475°C. 2. Cu-, or Mn-, Co-, or Fe-promoted (or combinations thereof) Pt - ceria-zirconia, Pt-ceria-lanthana, or Pt-ceria catalysts with high WGS activity and no methane formation over a large temperature range (200-600°C). 3. Impact of the preparation method of La-doped ceria for suppression of methanation reaction (estimated to be due to a lanthanum carbonate/hydroxy-carbonate phase). 4. Use of CuOx-CeOx oxides for WGS.

Benefit of Invention:

1. Catalyst formulations with high WGS catalytic activity and with no methanation activity over a large temperature range. 2. Suppression of methane formation on platinum-ceria-zirconia, or platinum-ceria-lanthana, or platinum-ceria, under WGS reaction conditions, by promotion with Cu, Mn, Co, Fe or combinations thereof.

References to Supporting Work (e.g. Lab Notebook Number): most significant data is listed

1757-132-3	(1%Pt-0.5%Cu)/75%La2O3-25%CeO2
1757-138-3	(1%Pt-0.5%Cu)/ 25%La2O3-75%CeO2
1757-145-13	(1%Pt-0.5%Cu)/CeO2
1757-144-15	(1%Pt-0.5%Cs-0.5%Cu)/CeO2 (also refer to previous WGS Rol - here combined effect Cs-Cu)
C480-96A	1%Pt/LaOx-CeOx -
1757-4-149-1A	1%Cu/2.5%Pt/CeO2 -
1757-4-149-2A	0.5%Cu/2.5%Pt/CeO2 -
1757-4-149-3A	2.5%Cu/2.5%Pt/CeO2 -
1875-001	(1%Pt-5%Cu)/CeO2 -
1875-002	(1%Pt-10%Cu)/CeO2 -
1875-003	10%Cu/CeO2 -
1875-007	CuOx-CeOx (Cu:Ce ~20:80 wt) -
1875-011	CuOx-CeOx (Cu:Ce ~50:50 wt) -
1757-188A	2%Pt/Fe-CeO2 -
1944-001	2%Pt/0.2%Cu/CeO2-ZrO2 (19.6 : 80.4 wt) -
1944-017	2%Pt/0.2%Cu/CeO2-ZrO2 (58 : 42 wt) -
1944-019	0.2%Cu/2%Pt/CeO2-ZrO2 (58 : 42 wt) -

1944-011	10%Cu/ CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-003	2%Pt/0.6%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-057	2%Pt/1%Co/CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-021	2%Pt/0.2%Cu/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-023	0.2%Cu/2%Pt/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-029	10%Cu/ CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1875-031	2%Pt/(ZrO _x —CeO _x -MnO _x)
1944-025	2%Pt/0.5%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-033	2%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-035	2%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-037	3%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-039	3%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-041	2%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-043	3%Pt/0.2%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-045	3%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-047	2%Pt/0.1%Mn/CeO ₂ -ZrO ₂ (19.6 : 80.4 wt) –
1944-079	2%Pt/2%Co/CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-081	2%Pt/1%Fe/CeO ₂ -ZrO ₂ (58 : 42 wt) –
1944-083	2%Pt/(0.5%Fe-0.25%Mn)/CeO ₂ -ZrO ₂ (58 : 42 wt) –

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If Invention has been discussed with or disclosed to external third parties, give details:
Discussed with GM.

Witness Statement:

"On the date beside my signature, I read and understood the above invention"

Name: _____

Signature: _____

Date: _____